Application of ultrasound and air stripping for the removal of aromatic hydrocarbons from spent sulfidic caustic for use in autotrophic denitrification as an electron donor

Jae-Ho Lee, Jeung-Jin Park, Gi-Choong Choi, Im-Gyu Byun, Tae-Joo Park and Tae-Ho Lee

ABSTRACT

Spent sulfidic caustic (SSC) produced from petroleum industry can be reused to denitrify nitrate-nitrogen via a biological nitrogen removal process as an electron donor for sulfur-based autotrophic denitrification, because it has a large amount of dissolved sulfur. However, SSC has to be refined because it also contains some aromatic hydrocarbons, typically benzene, toluene, ethylbenzene, xylene (BTEX) and phenol that are recalcitrant organic compounds. In this study, laboratory-scale ultrasound irradiation and air stripping treatment were applied in order to remove these aromatic hydrocarbons. In the ultrasound system, both BTEX and phenol were exponentially removed by ultrasound irradiation during 60 min of reaction time to give the greatest removal efficiency of about 80%. Whereas, about 95% removal efficiency of BTEX was achieved, but not any significant phenol removal, within 30 min in the air stripping system, indicating that air stripping was a more efficient method than ultrasound irradiation. However, since air stripping did not remove any significant phenol, an additional process for degrading phenol was required. Accordingly, we applied a combined ultrasound and air stripping process. In these experiments, the removal efficiencies of BTEX and phenol were improved compared to the application of ultrasound and air stripping alone. Thus, the combined ultrasound and air stripping treatment is appropriate for refining SSC.

Key words | air stripping, aromatic hydrocarbons, autotrophic denitrification, spent sulfidic caustic, ultrasound irradiation

INTRODUCTION

Sodium hydroxide (NaOH) solutions are often used in the oil refining industry for desulfurization from hydrocarbon streams. Once hydrogen sulfide reacts with the majority of NaOH in the solution, the solution becomes known as spent sulfidic caustic (SSC). Thus, SSC typically has a large amount of sulfide, as well as a high concentration of alkalinity due to the formation of caustic soda. Without treatment, these streams may impose environmental problems because of their high sulfide levels, alkalinity and salinity.

Research has been conducted on the eco-friendly reuse of SSC as an alternative carbon source for autotrophic denitrification (Park et al. 2008). However, depending on the source, SSC contains some aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, xylene (BTEX) and phenol. In wastewater treatment, BTEX and phenol are classified as priority water pollutants and they are recalcitrant organic compounds. For this reason, the injection of SSC to the biological nitrogen removal process induced an increase of chemical oxygen demand (COD) in the effluent (Park et al. 2008). Thus, SSC has to be refined for removal of aromatic hydrocarbons and for the stable injection into a wastewater treatment process.

Ultrasound has been extensively used as an advanced oxidation process (AOP) for wastewater treatment because it has been demonstrated as a promising method for the destruction of aqueous pollutants (Guo et al. 2008). The passage of ultrasound through a liquid induces physical and chemical processes, largely through acoustic cavitation (Crum 1995). Intense sound waves traveling through a

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liquid during expansion cycles produce cavitation bubbles. The rapid collapse of the bubbles adiabatically compresses the gas and entrapped vapor, producing small local hot spots. At the final step of the bubble collapse, the temperature and pressure inside the residual bubble increase up to 5,000 K and in a range of 500 ~ 1,000 atm, respectively. Under such extreme conditions the solvent molecules undergo hemolytic bond breakage to generate radicals. When water is sonicated, H· and OH· radicals are produced (Riez et al. 1990). These primary radicals of sonolysis can react with organic pollutants and thus enable bond transformations or homolysis of organic compounds dependent on their respective volatilities. Alternatively, organic compounds in the vicinity of a collapsing bubble may undergo pyrolytic decomposition due to the local high temperature and pressure (Suslick 1986).

BTEX contained in SSC are volatile organic compounds (VOCs) which are easily vaporized. This means that most recalcitrant organic compounds of SSC can also be removed through the air stripping process. During aeration, oxygen is transferred into solution, while the pre-dissolved VOCs are emitted to the atmosphere from the solution (Hsieh 2000).

In this study, to reuse SSC as an electron donor for sulfur-based autotrophic denitrification, we applied ultrasound irradiation and air stripping to remove BTEX and phenol from SSC and compared the removal efficiency by the two methods. Ayyildiz et al. (2005) reported that combining ultrasound with air stripping could yield beneficial mass transfer effects of acoustic waves contributing to greater removal rates of organic compounds from liquid. Thus, we evaluated the synergy of combined ultrasound and air stripping treatment in the removal of BTEX and phenol from SSC.

**METHODS**

**Characteristics of SSC**

The characteristics of SSC used in this study are presented in Table 1. SSC contains high concentration of sulfide and alkalinity with 17,983 and 68,000 mg/L, respectively, making it possible to be used for autotrophic denitrification. SSC also has some aromatic hydrocarbons such as BTEX and phenol. Of these organic compounds, benzene and xylene turned out to be the dominant aromatic hydrocarbon with a concentration of 57.75 and 159.15 mg/L, respectively. These organic compounds are classified as recalcitrant organic compounds and thus can induce an increase in COD concentration when SSC is used for autotrophic denitrification in the biological nitrogen removal process. In order to remove aromatic hydrocarbons, ultrasound and air stripping were used.

**Experimental apparatus**

Experiments for the removal of aromatic hydrocarbons by ultrasound irradiation were performed using an ultrasound processor manufactured by Sonics and Materials, Inc. (VC 750, 20 kHz and 750 W of nominal power, USA). A 2.5 cm diameter metal probe (CV33, 28 cm long, USA) was connected to the transducer and dipped directly into the solution. Experiments were performed in 2 L of air-tight reactor made of stainless steel with a Teflon cover. The reactor was fixed in the water bath (WCR-12, temperature range -40 to 100 °C, Daihan, Korea) to evaluate the effect of temperature on ultrasound. Water level inside the bath was maintained by continuous circulation of water. For air stripping and the combined ultrasound and air stripping experiments, a membrane air diffuser connected to an air blower was installed in the reactor, as shown in Figure 1. Air flow rate was adjusted to 10 L/min for all experiments. The reactor has five ports for the ultrasound: probe, inlet and outlet gas flow, sampling, thermometer. They were sealed with Teflon valves and covered with rubber septa.

**Experimental procedure**

For the ultrasound and air stripping experiments, 1 L of SSC was placed in the reactor. The initial test was...
performed irradiating different ultrasound power of 400 ∼ 600 W to evaluate the effect of power density. After choosing the power density, the effect of temperature was studied in the range of 20 ∼ 60 °C. For the evaluation of the removal of aromatic hydrocarbons by air stripping, 10 L/min of air was supplied without ultrasound irradiation. Finally, a combined ultrasound and air stripping test was performed to evaluate the synergistic effect by those two methods.

For each 10 min sampling, treated liquid sample was withdrawn from the reactor using a sampling syringe equipped with a 20 cm needle. BTEX were subsequently analyzed using an HP 6890 purge and trap gas chromatograph mass spectrometer equipped with an auto sampler, flame ionization detector and a column (HP5, 30 m × 250 μm × 1 μm, USA). Phenol concentration was determined by high performance liquid chromatograph (Waters model 515, USA). Detection was made at 250 nm with a model 486 absorbance detector and the column was a Supelcosil LC-18 column (4.6 mm × 250 mm). The sulfur content was measured using an inductively coupled plasma atomic emission spectrophotometer (Thermo Jarrell Ash, USA).

RESULTS AND DISCUSSION

Removal efficiencies of aromatic hydrocarbons by ultrasound

Effect of power density

To evaluate the effect of ultrasound power density, 400, 500 and 600 W of ultrasound power with a solution of 1 L at 20 °C was supplied. The concentrations of benzene and phenol with reaction time under three different ultrasound powers are shown in Figure 2(a). After 60 min of ultrasound irradiation, the removal efficiencies of benzene were 70.7, 75.4 and 80.6% and those of phenol were 56.0, 59.6 and 60.9% at ultrasound powers of 400, 500 and, 600 W, respectively.

Some studies reported that the degradation rates of benzene and phenol by ultrasound follow a pseudo-first-order kinetic law (Goel et al. 2004). In these experiments, benzene and phenol were exponentially removed by ultrasound irradiation, indicating that the degradation rate using ultrasound irradiation followed a pseudo-first-order kinetic model, as described by Equation (1).

\[
C_t = C_0 \cdot e^{-kt}
\]

where, \(C_0\) is the initial concentration, \(C_t\) is the concentration at sonication time (t) and \(k\) is the rate constant.

The pseudo-first-order rate constants (k) of benzene were 0.0204, 0.0235, 0.0272 min \(^{-1}\) and the k of phenol were 0.0142, 0.0151, 0.0158 min \(^{-1}\) at the ultrasound power density of 400, 500, 600 W, respectively. These results showed that the degradation rates of both benzene and phenol were found to increase with the increase of power density. In the ultrasound system, the degradation of
compounds is due to the phenomenon of cavitation which is the nucleation, and the behavior of bubbles in a liquid. A greater ultrasound power density induced the formation of more cavitation bubbles (Manousaki et al. 2004) and hence increased the degradation rate of organic compounds. Thus, the \( k \) of benzene and phenol gradually increased with increasing ultrasound power.

As shown in Figure 2(b), benzene degrades more rapidly than phenol. When volatile and non-volatile compounds are simultaneously degraded by ultrasound irradiation, the more volatile compounds degrade first, thus disturbing decomposition of the non-volatile compound (Pétrier et al. 1998). As shown in Table 1, SSC contains a high concentration of volatile compounds such as BTEX. Therefore, it is considered that the degradation of phenol was inhibited by BTEX.

**Effect of temperature**

In an ultrasound reactor, the temperature increases rapidly with sonication if it is not controlled. Thus, it is possible to make use of the advantage of temperature rise in a sonochemical reactor if the temperature has a positive effect on the degradation rate constant. The \( k \) values of benzene and phenol according to temperature at a fixed ultrasound power of 600 W at 1 L are given in Figure 3. The \( k \) values of benzene were 0.0253, 0.0296 and 0.0322 min\(^{-1}\) and those of phenol were 0.0154, 0.0147 and 0.0144 min\(^{-1}\) at temperatures of 20, 40 and 60 °C, respectively. These results showed that the removal efficiencies of benzene increased with increasing temperature, whereas those of phenol decreased with increasing temperature. Volatile compounds tend to predominantly degrade via pyrolytic and combustive reactions within the bubble–liquid interfacial region and collapsing cavitation bubble, while non-volatile compounds tend to accumulate in the liquid phase, where they are oxidized by the OH radical (Psillakis et al. 2004). When the temperature increases, more benzene molecules are evaporated and have more chance to undergo pyrolytic reactions at the interfacial region and in the cavitation bubble (Neppolian et al. 2002). Thus, the degradation of benzene is positively correlated with temperature. Phenol, a non-volatile organic compound, is barely evaporated by degassing with increased temperature. Psillakis et al. (2004) reported that increased temperatures are likely to favor degassing of the liquid phase, thus reducing the number of gas nuclei available for bubble formation. Phenol is removed via hydroxyl radical reactions in the bubble/water interfacial. Therefore, the decreased number of bubbles reduced the removal efficiency of phenol.

**Degradation rate of BTEX**

The removal efficiencies of BTEX by ultrasound irradiation with ultrasound energy input of 600 W/L at 20 °C are shown in Figure 4(a). After 60 min of ultrasound irradiation, the removal efficiencies of BTEX were 79.2, 82.4, 84.9 and 77.8%, respectively. The degradation rates of BTEX were represented in Figure 4(b) and followed a pseudo-first-order kinetic model. The \( k \) of BTEX were 0.0265, 0.0286, 0.0309 and 0.0252 min\(^{-1}\), respectively, indicating that the degradation rate of ethylbenzene was the...
Table 2 | Henry’s law constant of BTEX

<table>
<thead>
<tr>
<th>Items</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>o-Xylene</th>
<th>m-Xylene</th>
<th>p-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry’s law constant (atm m³ mol⁻¹)</td>
<td>5.43 × 10⁻³</td>
<td>6.61 × 10⁻³</td>
<td>7.9 × 10⁻³</td>
<td>5.19 × 10⁻³</td>
<td>7.66 × 10⁻³</td>
<td>7.66 × 10⁻³</td>
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greatest. The major decomposition of BTEX takes place dominantly inside collapsing bubbles by direct pyrolysis. The availability of the pyrolysis reaction in BTEX bubbles may be significantly associated with substrate transport from the bulk phase into the gaseous. Therefore, the magnitude of Henry’s law constant is strongly associated with the solute transfer rate from the bulk into the cavity (Kang et al. 2001). As shown in Table 2, ethylbenzene had the highest Henry’s law constant, which contributed to the greatest mass transport of ethylbenzene into the bubble and the highest removal efficiency. Xylene had a higher Henry’s law constant than benzene, but the k of benzene was greater than that of xylene. Although the major degradation route of BTEX is pyrolysis in the cavity or in the interfacial region, BTEX can also be decomposed by OH radical reaction. Pyrolysis was the predominant pathway at high solute concentration, compared to OH radical reaction at low initial substrate concentration (Kang et al. 2001). Thus, OH radical reaction may have a greater effect on the removal of benzene than xylene, which explains the greater degradation rate of benzene than that of xylene.

Removal efficiencies of aromatic hydrocarbons by combined ultrasound and air stripping

Ultrasound, air stripping and combined ultrasound and air stripping treatment of benzene and phenol from SSC were evaluated based on the removal efficiency. The objective of this experiment was to examine the synergy of combined ultrasound and air stripping treatment in the removal of BTEX and phenol. The removal efficiencies of benzene and phenol by ultrasound, air stripping and combined ultrasound and air stripping treatment were given in Figure 5. For the experiments of air stripping at 10 L/min, after 30 min, approximately 95% of benzene was removed. On the other hand, phenol was hardly removed by air stripping because of its low Henry’s law constant. For the experiments of ultrasound at 600 W/L, the removal efficiencies of benzene and phenol were about 81 and 60% after 60 min of ultrasound irradiation, respectively. These results show that the removal efficiency of benzene by air stripping was much greater than that by ultrasound irradiation alone because benzene is a highly volatile compound, whereas phenol was more effectively degraded by the ultrasound irradiation than air stripping. Although air stripping was an effective method to remove volatile compounds, it had no significant effect on the removal of phenol. The removal efficiency of phenol by ultrasound irradiation was significant, but it is also much lower than that of benzene. Thus, we conducted the experiment using combined ultrasound and air stripping treatment. In this experiment, both benzene and phenol were degraded more rapidly than using ultrasound and air stripping alone. In the case of benzene, although about 95% of benzene was removed by combined ultrasound and air stripping treatment within 20 min, it did not show a synergistic effect because benzene was predominantly removed by air stripping. However, combined ultrasound and air stripping treatment had a synergistic effect on the removal of phenol. After 60 min of combined ultrasound and air stripping treatment, the removal efficiency of phenol exceeded the sum of the individual removal efficiencies with ultrasound and air stripping. In the ultrasound system with no air stripping, the generation of OH radicals only arises from the cavitation induced dissociation of water. On the other hand, under an oxygen atmosphere, additional OH radicals are generated by molecular oxygen dissociation in the bubble (Pétrier et al. 2007). Thus, phenol undergoes faster degradation as a result of the increased available OH radicals in the liquid around the cavity.

In order to apply the combined ultrasound and air stripping process for refining SSC practically, stripping air
produced after the process has to be discharged into the air after treatment because it can also contain aromatic hydrocarbons and hydrogen sulfide. However, in the case of hydrogen sulfide, it is thought to be hardly detected in stripping air because the type of sulfur in SSC is sulfide which is not removed by air stripping. Generally, polluted gas can be refined by several types of processes such as oxidation and adsorption. Thus, the thermal oxidation system and activated carbon tower could be considered a post-process for removing aromatic hydrocarbons from polluted gas.

CONCLUSIONS

The application of SSC for reuse as an alternative carbon source in a wastewater treatment process without any further refining is inadequate because SSC contains some aromatic hydrocarbons that may harm the activated sludge and increase the effluent COD. The most common aromatic hydrocarbons of SSC are BTEX and phenol. To remove these organic compounds, we applied ultrasound and air stripping methods. In the ultrasound system, BTEX and phenol were exponentially removed by ultrasound irradiation during 60 min of reaction and followed a pseudo-first-order kinetic model. The rate of BTEX removal increased with increasing ultrasound power density, temperature and Henry’s law constant, giving the greatest removal efficiency of 85% for ethylbenzene. However, the rate of phenol degradation decreased with increasing temperature. In air stripping treatment, the removal efficiency of BTEX were about 95% within 50 min of aeration, indicating that air stripping was more efficient than ultrasound irradiation for removing BTEX. However, since air stripping does not have a significant effect on removing phenol, additional processing for degrading the phenol is required. Accordingly, we applied combined ultrasound and air stripping treatment. In these experiments, the removal efficiency of BTEX and phenol were improved compared to the application of ultrasound and air stripping alone. Thus, the combined ultrasound and air stripping treatment process is appropriate for refining SSC.

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